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IN THE CASE OF RESONANCE QUENCHING

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ON THE THEORETICAL DERIVATION OF THE LAW
OF SCINTILLATION DECAY IN THE CASE OF
RESONANCE QUENCHING

by

V. V. Antonov-Romanovskiy and M. D. Galanin

B. Ya. Svashnikov in a note [1] expressed some critical remarks concerning the theoretical derivation of the law of scintillation decay in the case of concentrated (or, generally, resonance) quenching given in works by Förster [2] and Galanin [3]. Unfortunately, these critical remarks were based on a misunderstanding. Here we give a more detailed derivation [3] performed according to a method proposed by one of us [4], since the misunderstanding was apparently caused by the shortness of the description in [3].

Let us assume that the quenching of the luminescence of a solution occurs as a result of the inductive-resonance transfer of the energy of excitation from excited molecules to unexcited ones. In the case of a dipolar interaction the probability of a transfer in a unit of time from an excited molecule to one being quenched at a distance R is determined by the expression (after averaging for orientation)¹⁾:

$$f(R) = \frac{1}{\tau_0} \left(\frac{R_0}{R} \right)^6, \quad (1)$$

where τ_0 is the average life in the absence of quenching and R_0 is a constant which depends on the properties of the interacting molecules. If the viscosity of the medium is sufficiently great in order to ignore the displacement of the molecules during the time of the excited state, then as a

1) In [3] the averaging for orientation was done more strictly which gives the slight correction which is omitted here for simplicity.

consequence of the sharp dependence of the probability of transfer on the distance a phenomenon occurs which in [4] is called "impoverishment": the probability of transfer averaged with respect to the excited molecules changes with time since the more favorable configurations of the quenching molecules with respect to the excited molecules are used first. Such is the physical reason why the law of the scintillation decay should be non-exponential in the case of resonance quenching.

In order to derive the law of scintillation decay let us assume that the initial moment there are n_0 excited molecules and we will write a kinetic equation for the number of excited molecules $n(t)$. In this, in order to consider the effect of "impoverishment," there is no need at all to consider the fluctuations of the density of the quenching molecules as has apparently been assumed by Sveshnikov. Actually, only the average magnitudes [3] figure everywhere in the derivation of the law of scintillation decay. Thus let us assume that the density of the quenching molecules about the excited molecules at the initial moment is generally uniform and equal to N_0 . Let us designate $N(R, t)dv$ as the average number of quenching molecules located in an element of a volume $dv = 4\pi R^2 dR$ at a distance between R and $R + dR$ from the excited molecules at the moment of time t . Then for the change of $n(t)$ with respect to time we will obtain

$$\frac{dn(t)}{dt} = - \left\{ \frac{1}{\tau_0} + \int_0^{\infty} N(R, t) f(R) dv \right\} n(t). \quad (2)$$

How does $N(R, t)$ change? The effect of "impoverishment" lies in the fact that $N(R, t)$ diminishes with time more rapidly as R becomes less. The equation for $N(R, t)$ can be written without introducing the function of $n(R, t)$ [3] and the member $f(R)n(R, t)dt$ which Sveshnikov considers incomprehensible (see the footnote in [1]).

Inasmuch as $N(R, t)$ is not simply the number of quenching molecules but rather the average number of quenching molecules averages with respect to an assembly of excited molecules $n(t)$, the diminution of $N(R, t)$ is based only on the transfer of the energy of excitation with the probability of (1), i.e.,

$$\frac{dN(R, t)}{dt} = -f(R) N(R, t). \quad (3)$$

Consequently,

$$N(R, t) = N_0 e^{-f(R)t}. \quad (4)$$

Upon substituting in (2) and integrating we will obtain

$$n(t) = n_0 e^{-\frac{t}{\tau_0} - N_0 \int_0^t (1 - e^{-f(R)s}) ds} \quad (5)$$

or, upon substituting (1),

$$n(t) = n_0 e^{-\frac{t}{\tau_0} - 2q \sqrt{\frac{t}{\tau_0}}}, \quad (6)$$

where q is a constant which depends on R_0 [2,3]. Formula (6) coincides with that obtained by Förster [2].

Thus the derivation of the scintillation decay is very simple and sufficiently clear. Within the framework of the physical assumptions which were made there is hardly any basis for considering it to be unfounded as was the case in [1].

Let us now examine Sveshnikov's objection to Förster's conclusion [2]. Förster derives the same law of decay in a somewhat different way. He considers first some definite configuration N of the quenching molecules about some excited configuration and then proceeds to perform an averaging with respect to such configurations. It is natural that in this case the law of decay for a given excited molecule is exponential while a non-exponential

condition occurs as a result of the averaging of the exponents and not of the probabilities. Therefore, Sveshnikov is completely wrong when he considers that within the framework of Förster's method, it is necessary to conduct the averaging already in the initial kinetic equation (the formula (13) in [1]). Sveshnikov's other objection is also incorrect where he asserts (without proof) that Förster's formula

$$\overline{\rho(t)} = e^{-\frac{t}{\tau_0}} \prod_{k=1}^N \int_0^{R_k} e^{-\left(\frac{R_0}{R_k}\right)^6 \frac{t}{\tau_0}} w(R_k) dR_k \quad (7)$$

is incorrect and that it "obviously" should be replaced by the formula

$$\overline{\rho(t)} = \frac{1}{n_0} e^{-\frac{t}{\tau_0}} \sum_{i=1}^{n_0} \prod_{k=1}^N e^{-\left(\frac{R_0}{R_{ki}}\right)^6 \frac{t}{\tau_0}} \quad (8)$$

However, from (7) and (8) it follows that for a sufficiently large n_0 (8) coincides with (7). For a sufficiently large n_0 the sum can be replaced by an integral if with the help of multiplier $w(R_k) dR_k$ one considers the number of molecules located in the layer $R_k, R_k + dR_k$. Upon switching the signs of the integral and the derivative which is possible inasmuch as the variables in the expression under the integral are distinguished, we will obtain (7). Thus Sveshnikov's objection applies essentially not to the derivation given by Förster but rather to an ordinary method applied in statistical physics.

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